Electronic Supplementary Material (ESI) for Materials Horizons

Supplementary Information for

Side-chain fullerene polyesters: a new class of high refractive index polymers

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Experimental Section

Chemicals.

4-Dimethylaminopyridine (DMAP), *p*-toluenesulfonic acid (PTSA) and *N*,*N*-diisopropylcarbodiimide (DIPC) was purchased from J&K and used without further purification. [60]Fullerene (99.9%) was purchased from Puyang Yongxin Fullerene Technology Co., Ltd. All reagents and chemicals were purchased from commercial sources (Aldrich, Across, Fluka) and used without further purification unless stated otherwise. Tetrahydrofuran (THF; Fluka) was distilled over Na / benzophenone. Pyridine (Py) was purified by vacuum distillation over calcium hydride. Anisole was washed twice with 10% aqueous sodium hydroxide solution, and then with water to neutral, dried over sodium sulfate and distilled over calcium hydride. 3,5-Bis-hydroxymethyl-phenol[1] (**7**) and [60]fullerenoacetic acid (**3**) were synthesized according to references.[2,3]

Measurements

The ^1H NMR spectrum was recorded on an INOVA 400 MHz nuclear magnetic resonance instrument using $CDCl_3$ as the solvent and tetramethylsilane (TMS) as an internal standard. Time-of-flight mass spectra were recorded with a Kratos MALDI-TOF mass system. Thermogravimetric analysis (TGA) was performed at a heating rate of 10 °C min^{-1} from room temperature to 800 °C under a continuous nitrogen flow of 50 mL min^{-1} with a SDT-2960TG/DTA TA instrument. The temperature of thermal degradation (T_d) was measured at the point of 5% weight loss relative to the weight at room temperature. The number-average molecular weight (M_n) and molecular weight distribution ($M_\mathrm{w}/M_\mathrm{n}$) of the resulting polymers were measured using a Waters 1515 gel permeation chromatograph (GPC) equipped with a refractive-index detector (Waters 2414), using HR 1, HR 2 and HR 4 (7.8×300 mm, 5 μm beads size) columns with molecular weights ranging from 10^2 to 5×10^5 g/mol. THF or $CHCl_3$ was used as the eluent at a flow rate of 1.0 mL/min and operated at 30 $^\mathrm{o}$C, calibrated with PS standards purchased from Waters. For UV-Vis spectra measurements, the solution (0.1 mg/mL) was prepared by dissolving 2.50 mg sample in 25.0 mL chloroform, filter with 0.45 μm filter, and the spectra were recorded on a Hitachi U-3900 spectrophotometer at room temperature. The normalized absorption intensity to fullerene concentration of 0.1 mg/mL was obtained by the absorption intensity divided with the fullerene content in the material. For FTIR measurements, samples were dispersed in potassium bromide and compressed into pellets, and spectra in the range of 400-4000 cm^{-1} were recorded with the Nicolet 6700 FT-IR Instrument.

For refractive index measurements, a spectroscopic ellipsometer (alpha-SE, J. A. Woollam Co.) equipped with a rotating compensator was used to measure the ellipsometric data Psi (Ψ) and Delta (Δ) of the polymer films. All measurements were performed between 400 nm and 900 nm at an angle of incidence Φ_0 of 70°, and all data were acquired and analyzed using CompleteEASE software version 4.46. Typically, samples were spin coated on the silica wafer from chloroform solution (10 mg/ml) at the rotating speed of 1000 RPM. For fullerene samples, the films were regarded as a homogeneous material with the thickness fitted by Cauchy dispersion relation in the limited wavelength range from 720 nm to 900 nm, where no light was absorbed by the material according to the UV-Vis results. After the film thickness was determined and fixed, the experimental data were fitted by the B-Spline layer combined with the Wavelength Range Expansion (WVL-EXPAND) Fit. Subsequently, in order to guarantee the results physical, the initial B-Spline layer optical constant was parameterized by the Gen-Osc layer, in which Gaussian oscillators were used to match the optical constant curve shapes.[4,5] Eventually, the optical constant data, including refractive indices (*n*), were obtained in the Gen-Osc layer. For films without fullerene, data were fitted only by the Cauchy dispersion layer, since the material is transparent in the wavelength from 400 to 900 nm.

Synthesis of (3,5-bis(hydroxymethyl)phenyl 6-bromohexyl)ether (3)

K_2CO_3 (6.48 g, 47.0 mmol) was added to a solution of 3,5-bis-hydroxymethyl-phenol (1.57 g, 10.2 mmol) and 1,6-dibromohexane (12.65 g, 51.85 mmol) in acetone (150 mL), and the suspension was kept for 6 h at reflux temperature. After cooling to RT, the salts were filtered. The solvent of the solution was evaporated under reduced pressure. Sample **3** (1.38 g, 66%) was obtained through silica gel column chromatography using petroleum ether / ethyl acetate (1/1, v/v) as eluent. mp = 76-77 °C . ^{1}H NMR (400MHz, $CDCl_3$) δ (ppm): 6.84 (s, 1H), 6.75 (s, 2H), 4.55 (s, 4H), 3.93 (t, 2H), 3.41 (t, 2H), 2.89 (s, 2H), 1.86 (m, 2H), 1.77 (m, 2H), 1.48 (m, 4H).

Synthesis of (3,5-bis(hydroxymethyl)phenyl hexyl)ether (2)

This compound was prepared with the same procedure as **3** using 1-bromohexane instead of 1,6-dibromohexane. ^{1}H NMR (400 MHz) δ (ppm): 6.90 (s, 1H), 6.82 (s, 2H), 4.64 (s, 4H), 3.96 (t, 2H), 2.01 (s, 2H), 1.77 (m, 2H), 1.45 (m, 2H), 1.30 (m, 4H), 0.91 (t, 3H).

Synthesis of (3,5-bis(hydroxymethyl)phenyl 6-azidehexyl)ether (4)

3 (0.50 g, 1.6 mmol) and sodium azide (1.02 g, 15.8 mmol) were dissolved in 5 mL of dimethylformamide (DMF) and stirred at 60 ^{o}C for 24 h, then 150 mL ethyl acetate was added to the mixture and NaN_3 was filtered. The organic phase was washed with water and dried over anhydrous Mg_2SO_4. The crude mixture was concentrated and purified by column chromatography (SiO_2, petroleum ether / ethyl acetate (1/1, v/v)). ^{1}H NMR (400MHz, $CDCl_3$) δ (ppm): 6.91 (s, 1H), 6.83 (s, 2H), 4.64 (s, 4H), 3.97 (t, 2H), 3.28 (t, 2H), 1.92 (s, 2H), 1.78 (m, 2H), 1.64 (m, 2H), 1.47 (m, 4H).

Synthesis of 12-(propioloyloxy)dodecyl [60]fullerenoacetate (6)

To a solution of **5** (0.46 g, 0.59 mmol) in DMF and 1, 2-dichlorobenzene mixture solution, was added DMAP (0.07 g, 0.57 mmol), PTSA (0.11 g, 0.57 mmol), DIPC (0.10 g, 0.79 mmol) and 12-

hydroxydodecyl propiolate (0.15 g, 0.59 mmol) and the solution was stirred at room temperature for 2 h. The solution was filtered and the second component was collected by column chromatography using eluent of CS_2/toluene (15/1, v/v). The product was precipitated in methanol, filtered and dried in vacuum oven to yield a brown solid (0.45 g, 80%). ^1H NMR (400MHz, $CDCl_3$) δ (ppm): 4.81 (s, 1H), 4.48 (t, 2H), 4.20 (t, 2H), 2.88 (s, 1H), 1.88 (m, 2H), 1.69 (m, 2H), 1.55 (m, 4H), 1.31 (m, 12H).

Synthesis of 6-(1-(6-(3,5-bis(hydroxymethyl)phenoxy)hexyl)-1*H*-1,2,3-triazole-4-carboxylate)hexyl [60]fullerenoacetate (7)

To a mixture of **4** (159 mg, 0.569 mmol) and **6** (577 mg, 0.568 mmol) in 30 mL CH_2Cl_2 and 20 mL H_2O, was added $CuSO_4$•$5H_2O$ (14.8 mg, 0.059 mmol) and sodium ascorbate (35.2 mg, 0.178 mmol). The mixture was stirred for 3 days at room temperature, the organic layer was diluted with dichloromethane, and washed with water. The organic phase was dried over anhydrous Mg_2SO_4 and filtered. The crude mixture was concentrated and purified by column chromatography (CS_2 / ethyl acetate = 1/1, v/v). The product was dissolved in chloroform and precipitated in methanol to obtain a brown solid (50%). ^1H NMR (400MHz, $CDCl_3$) δ (ppm): 8.05 (s, 1H), 6.92 (s, 1H) , 6.83 (s, 2H) , 4.80 (s, 1H), 4.67 (d, 4H), 4.44 (m, 4H), 4.35 (t, 2H), 3.96 (t, 2H), 1.98 (m, 4H), 1.87 (m, 2H), 1.77 (m, 4H), 1.53 (m, 4H), 1.37 (m, 14H); ^{13}C-NMR($CDCl_3$): δ: 172.81, 166.71, 161.18, 159.67, 148.51, 146.05, 145.79, 145.46, 145.42, 145.37, 145.29, 144.93, 144.87, 144.79, 144.78, 144.61, 144.15, 143.92, 143.47, 143.29, 143.21, 143.17, 143.16, 143.07, 143.01, 142.63, 142.41, 142.29, 141.33, 141.12, 140.69, 140.44, 136.57, 127.46, 117.66, 112.30, 109.99, 70.84, 67.74, 66.88, 65.74, 65.34, 50.76, 39.37, 30.25, 29.79, 29.77, 29.72, 29.51, 28.96, 28.91, 28.88, 26.31, 26.14, 26.12, 25.69. Figure S1 is the MALDI-TOF spectra of monomer **7**. Calculated for $C_{91}H_{47}O_7N_3Na$ $(M+Na)^+$: 1316.33; Found:1316.30.

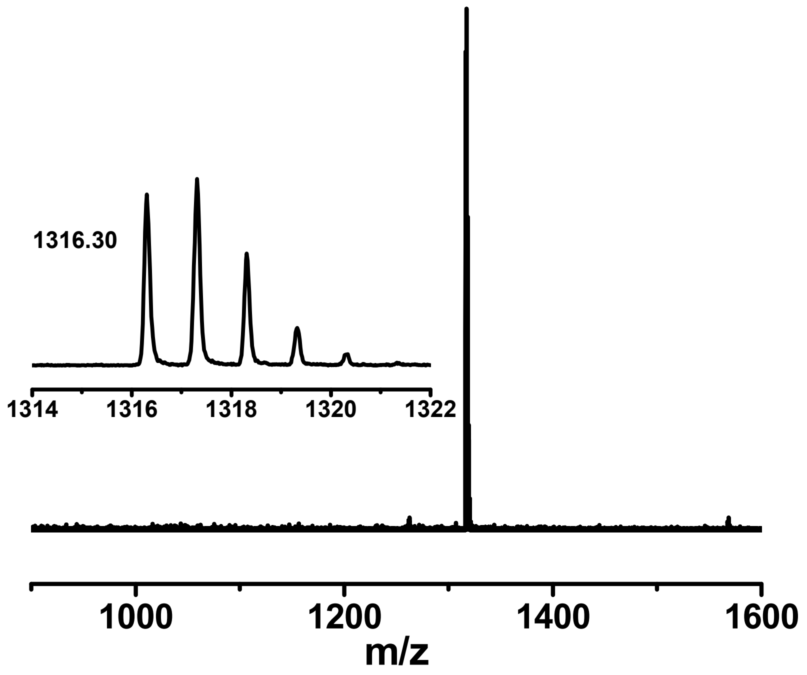


Fig. S1 MALDI-TOF mass spectra of monomer **7**.

Synthesis of polymer P1

Suberoyl chloride (51.8 mg, 0.264 mmol) was added to a solution of monomer 7 (318 mg, 0.260 mmol) and pyridine (44.8 mg, 0.566 mmol) in anisole (18 mL) at 0 °C. The resulting mixture was then allowed to slowly warm to 60 °C and stirred at this temperature for 24 h. The resulting materials was obtained by precipitating the solution in methanol. The oligomers and monomers was removed by precipitating again in THF to obtain dark red powder of polymer **P1** (108 mg, 32.63% yield). ^{1}H NMR (400 MHz): δ (ppm): 8.09 (s, 0.89H), 6.91-6.82 (m, 3.02H), 5.06 (s, 3.92H), 4.81 (s, 0.97H), 4.68 (s, 0.26H), 4.45 (m, 4.25H), 4.36 (t, 2.10H), 3.94 (t, 2.00H), 2.35 (m, 4.28H), 1.97-1.20 (m, 43.52H).

Synthesis of polymer P2

This compound was prepared with the same procedure as **P1.** ^{1}H NMR (400 MHz): δ (ppm): 8.08 (s, 0.84H), 6.89-6.79 (m, 2.85H), 5.05 (s, 4.01H), 4.80 (s, 0.94H), 4.67 (s, 0.08H), 4.44 (m, 4.21H), 4.35 (t, 2.15H), 3.93 (t, 2.00H), 2.37 (s, 4.32H), 1.9-1.2 (m, 41.55H).

Synthesis of polymer P3

This compound was prepared with the same procedure as **P1.** ^{1}H NMR (400 MHz): δ (ppm): 8.08 (m, 5.27H), 6.98 (m, 2.69H), 5.35 (t, 3.75H), 4.79 (s, 0.91H), 4.69 (s, 0.29H), 4.45 (m, 4.10H), 4.34 (s, 2.30H), 3.95 (s, 2.00H)**,** 2.00-1.25 (m, 38.21H).

Synthesis of polymer P4

This compound was prepared with the same procedure as **P1** with compound **2** as monomer. ^{1}H NMR (400 MHz): δ (ppm): 6.85 (m, 2.93H), 5.06 (s, 4.00H), 4.66 (s, 0.02H), 3.94 (t, 2.00H), 2.35 (t, 4.19H), 1.85-1.20 (m, 17.57H), 0.90 (t, 2.88H).

Number-average molecular weights (M_n) determination by ^{1}H NMR

Here we use polyester **P1** as an example to illustrate the determination of the molecular weights of the polymers. From Figure S2**,** since $I_{k'} + I_k < I_m$, we can deduce that there were coexisted polyesters with structure A as well as B, as shown in Scheme S1, where $I_{k'}$, I_k, I_m is the integral values of the peaks according to *k* (5.05 ppm), *k'* (4.67 ppm) and *m* (2.37 ppm) of polyester (**P1**), respectively.

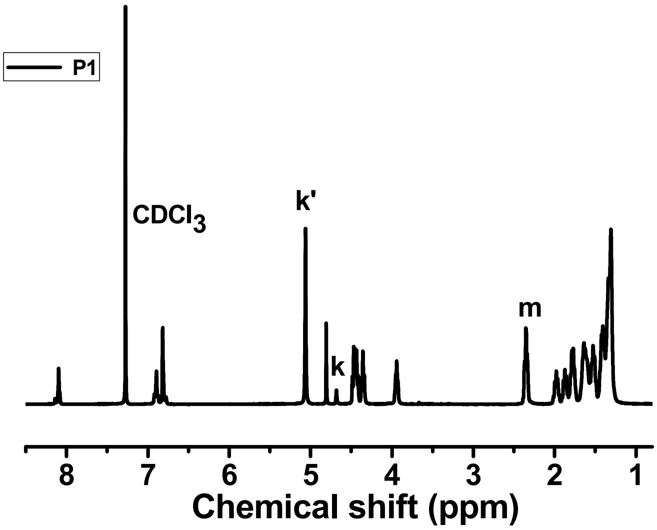
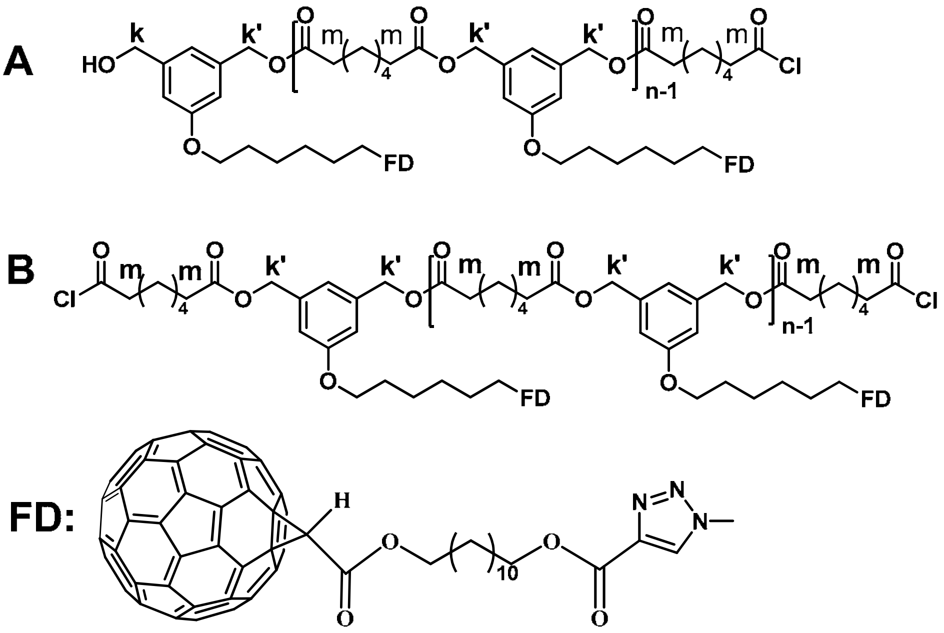


Fig. S2 ^{1}H NMR spectroscopy of **P1.** (solvent: $CDCl_3$).



Schemes S1 The chemical structures of polyester **P1** with different chain end.

According to the following equations (1), (2), (3), we can calculate number-average molecular weight of polyesters from integral values of ^{1}H NMR.

$$\frac{(4n-2)x+4ny}{2x}=\frac{I_{k'}}{I_k} \qquad (1)$$

$$x+y=1 \qquad (2)$$

$$\frac{4nx+4ny}{4nx+4ny+4y}=\frac{I_{k'}+I_k}{I_m} \qquad (3)$$

where n is the number of repeating units, x and y is the ratio of polyesters with structure A and B, respectively. Similar calculation can be applied to polymer **P2** and **P4**. The number-average molecular weights of **P1**, **P2** and **P4** estimated by ^{1}H NMR were 9720 g/mol, 14800 g/mol, and 6840 g/mol respectively.

For polyester P3, the following equations (4), (5), (6) was used to calculate molecular weight of **P3** from integral values of ^{1}H NMR (Figure S3). Because of the $(I_{k'}+I_k)/4 < I_{m+p}/5$, polyesters with structure C and D coexisted in **P3**, as illustrated in Scheme S2.

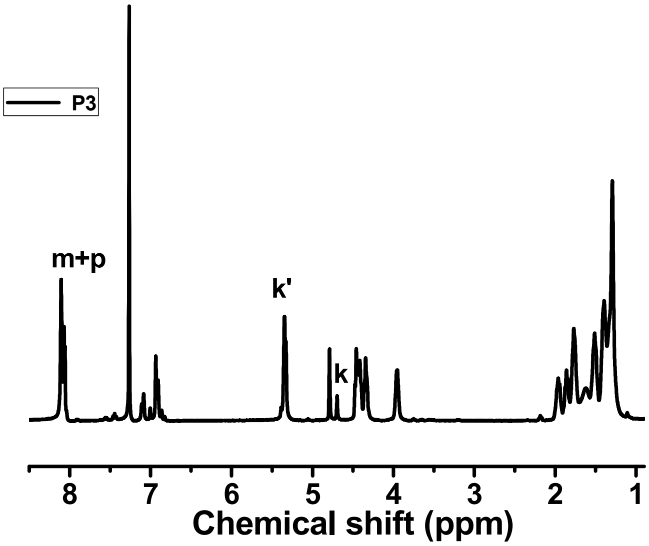
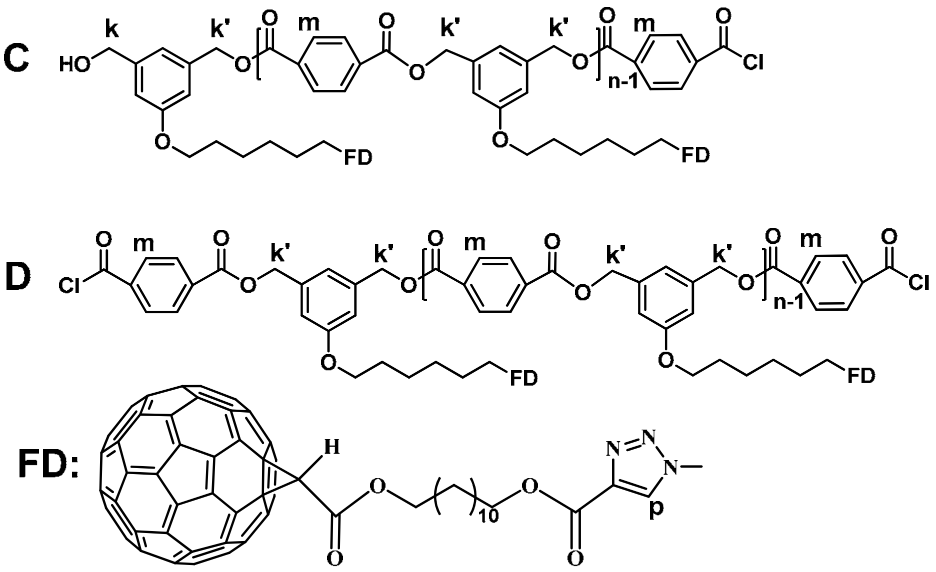


Fig. S3 ^{1}H NMR spectroscopy of **P3**. (solvent: $CDCl_3$).



Scheme S2 The chemical structures of polyester **P3** with different chain end.

$$\frac{(4n-2)x+4ny}{2x}=\frac{I_{k'}}{I_k} \qquad (4)$$

$$x+y=1 \qquad (5)$$

$$\frac{4nx+4ny}{5nx+5ny+4y}=\frac{I_k+I_{k'}}{I_{m+p}} \qquad (6)$$

where *n* is the number of repeating units, $I_{k'}$, I_k, $I_{m+\mathrm{p}}$ is the integral values of the peaks corresponding to 5.35 ppm, 4.67 ppm and 8.08 ppm of polyester (**P3**), x and y is the ratio of polyesters C and D. The number-average molecular weights of **P3** calculated by ^{1}H NMR was 7440 g/mol.

UV-Vis Spectra

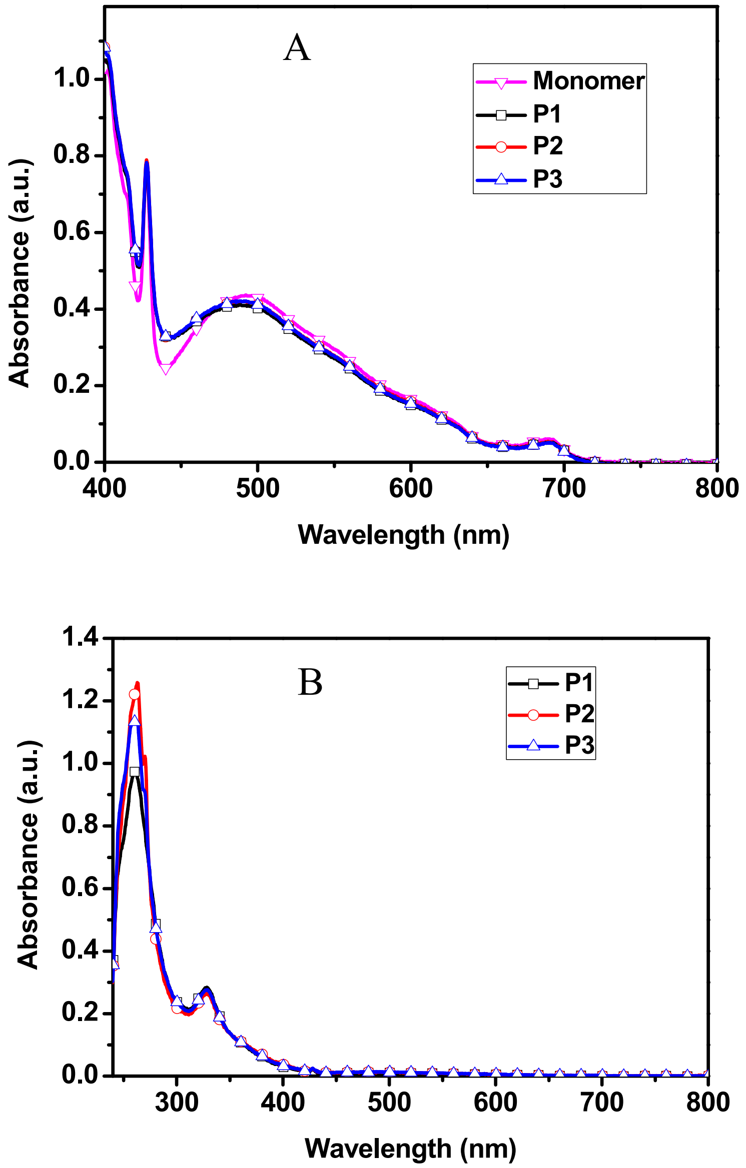


Fig. S4 UV-Vis spectra of monomer **7** and polyesters **P1~P3** in chloroform solution, at high C_{60} concentration (normalized to 1.00 × 10^{-4} g/mL), where the weak characteristic peaks (428 nm and 690 nm) of methano[60]fullerenes are observed (A), and at low C_{60} concentration (normalized to 5.0 × 10^{-6} g/mL), where the strong characteristic peaks (261 nm and 329 nm) of fullerenes are observed (B).

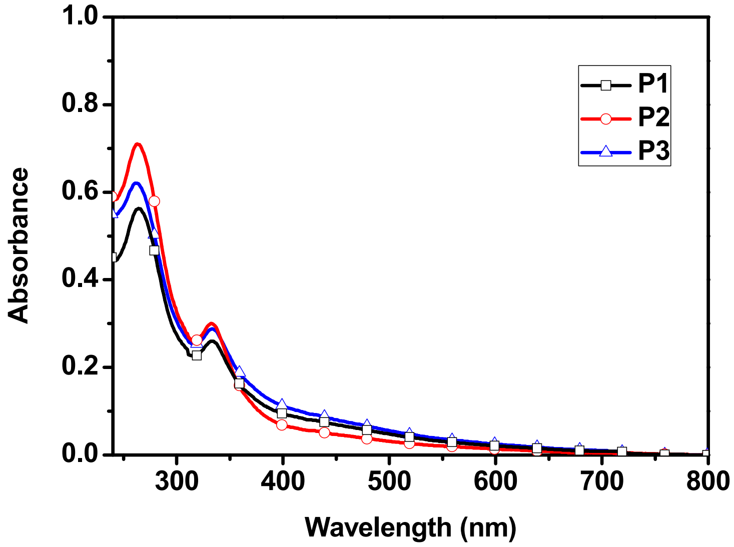


Fig. S5 UV-Vis film spectra of fullerene polyesters P1~P3. The strong characteristic absorption peaks for fullerenes are observed at 263 nm and 333 nm. The slightly red-shift of the film spectra compared to the solution is observed.

Thermogravimetric Analysis (TGA)

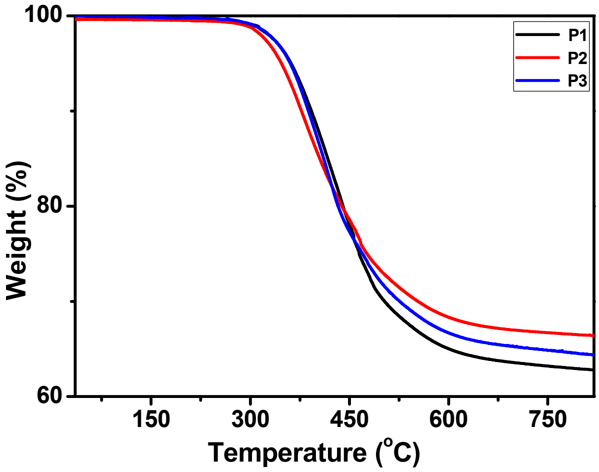


Fig. S6 TGA curves of **P1** (black line), **P2** (red line) and **P3** (blue line) under N_2. Heating rate 10 ^{o}C/min.

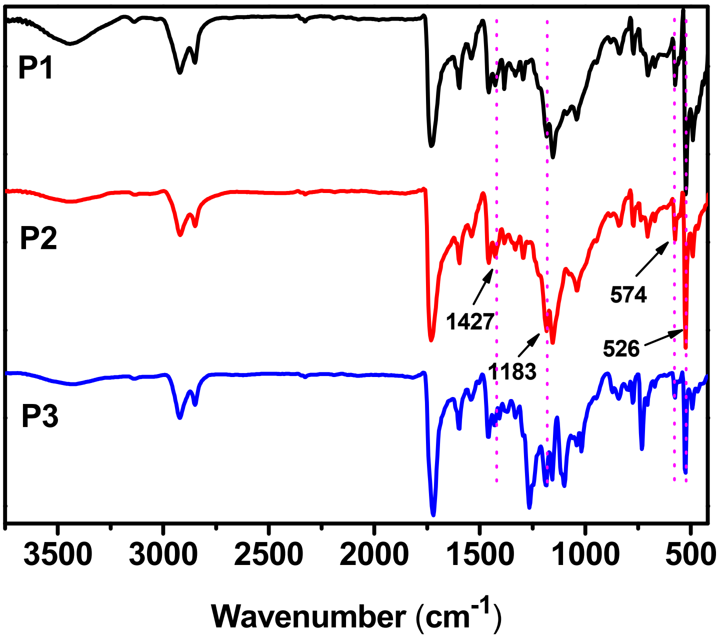


Fig. S7 FTIR spectra of fullerene polymers P1, P2 and P3. The dotted lines indicate the characteristic absorption peaks for fullerene (526 cm^{-1}, 574 cm^{-1}, 1183 cm^{-1} and 1427 cm^{-1}).

FTIR spectroscopy measurements were carried and the results are presented in Fig. S7. All three samples show the characteristic peaks at 526 cm^{-1}, 574 cm^{-1}, 1183 cm^{-1}, and 1427 cm^{-1}, which are attributed to strong intramolecular modes of C_{60}.[6] The peaks at 2920 cm^{-1} and 2850 cm^{-1} are correspondence to the C-H stretching of methylene groups, while the strong peak at 1730 cm^{-1} belongs to the carbonyl groups, and the peak at 1598 cm^{-1} to carbon-carbon stretching vibrations in the aromatic ring. The peak at 1460 cm^{-1} is attributed to the bending vibrations of CH_2 in the long alkyl chain. For P3, due to the high concentration of phenyl groups, it has stronger absorption peak at 731 cm^{-1}, which is from the out-of-plane C-H bending vibration of the para-substituted aromatic ring. These results strongly support the structure of obtained fullerene polymers as we presented in Scheme 1.

The fitting data for measured curves from ellipsometer:

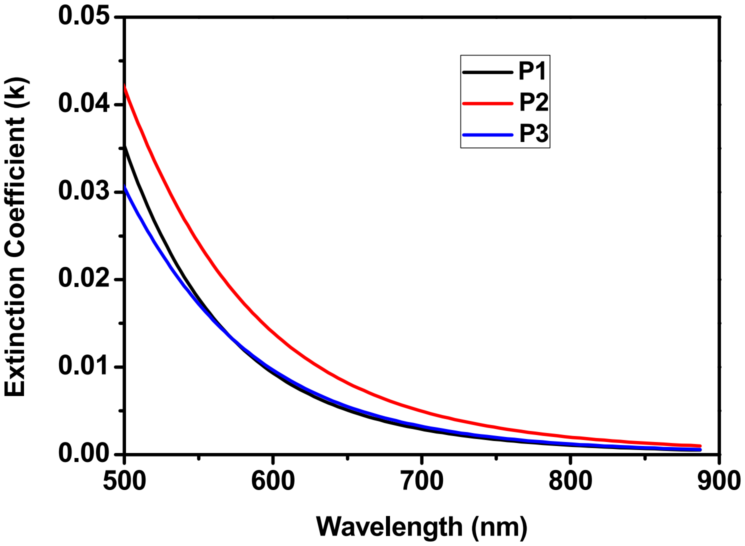


Fig. S8 Extinction coefficient (k) of polymers at different wavelength. **P1**: black line; **P2**: red line; **P3**:blue line. The film thickness of **P1**, **P2** and **P3** polymers is 49.5 nm, 55.6 nm and 48.0 nm, respectively.

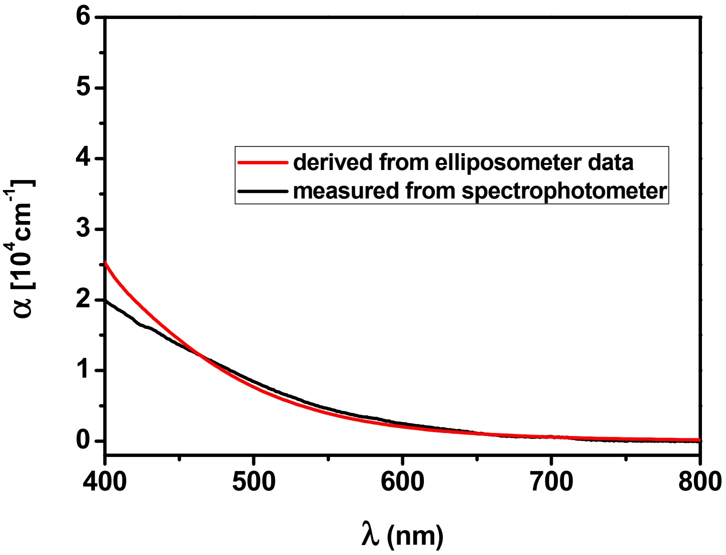


Fig. S9 Absorption spectra of P3 polymer derived from ellipsometer data (red line) by $\alpha = 4\pi k/\lambda$, where k is the extinction coefficient measured by ellipsometer, and directly measured using a spectrophotometer (black line) as referecne.[7] The good match of these two lines indicates the good reliabity of our data measured from elliposometer.

Theoretical refractive index calculation:

The Lorentz-Lorenz equation (equation 1 in the manuscript) is often used to predict the refractive index of an unknown polymer, and can be written as equation 7:[8]

$$\frac{n^2-1}{n^2+2}\frac{M}{\rho}=R_L=\sum_{j=1}^{J}k_jR_j \qquad (7)$$

where n is the refractive index, M is the molecular weight of the repeating unit, ρ is the density (g/cm^3), R_L is the molar refraction (cm^3/mol), k_j is the number of increments of the substructure j in the repeating unit, R_j is the molar refraction increment of substructure j (cm^3/mol), and J is the total number of individual substructures. According to the equation, the molar refraction R_L is equal to the sum of refraction increments R_j, each corresponding to a particular functional group within the polymer repeating unit.

The values of the refraction increments R_j for different functional groups used in this paper is listed in Table S1.

Table S1 Molar refraction increments R_j of different polymer substructures at Sodium D line (589 nm).[a]

No.	Group	R_j	No.	Group	R_j
1	CH_3	5.901	6	p-C_6H_4 (arom)	25.235
2	CH_2	4.504	7	C_6H_3 (arom)	24.785
3	CH	3.412	8[b]	Triazole	25
4	CO_2	6.289	9[c]	C_{60}	228.76
5	O(ether)	1.625			

[a] Data from the reference 6 unless specially mentioned. [b] The molar refraction increment value of triazole can not be found in any reference, and the value of benzene was used instead. [c] From the website: http://www.lookchem.com/-60-Fullerene

The molar refraction of the polymers is calculated from equation S1, and the refractive indices of polymers are calculated according to equation 1. The calculated values of molar refraction and refractive indices of the polyesters are listed in Table 2 in the manuscript.

References.

1 A. K. Jain, V. V. Reddy, A. Paul, K. Muniyappa, S. Bhattacharya, *Biochemistry*, 2009, **48**, 10693-10704.

2 Y. Wang, J. Cao, D. I. Schuster, S. R. Wilson, *Tetrahedron Lett.*, 1995, **36**, 6843-6846.

3 B. Ma, C. E. Bunker, R. Gudura, X.-F. Zhang, Y.-P. Sun, *J. Phys. Chem. A*, 1997, **101**, 5626-5632.

4 *Complete Ease^{TM} Data Analysis Manual, Version 3.65*; J. A. Woollam Co., Inc.: NE, 2008.

5 S. Rauch, K.-J. Eichhorn, U. Oertel, M. Stamm, D. Kuckling, P. Uhlmann, *Soft Matter*, 2012, **8**, 10260-10270.

6 W. Krätschmer, L. D. Lamb, K. Fostiropoulos and D. R. Huffman, *Nature*, 1990, **347**, 354-358.

7 F. Fitrilawati, M.O. Tjia, S. Pfeiffer, H.-H. Hörhold, A. Deutesfeld, H. Eichner, C. Bubeck, *Opt. Mater.*, 2002, **21**, 511-519.

8 W. Groh, A. Zimmermann, *Macromolecules*, 1991, **24**, 6660-6663.